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(21) International Application Number: PCT/US95/02699 (22) International Filing Date: 1 March 1995 (01.03.95) (30) Priority Data: 9406543.0 31 March 1994 (31.03.94) GB (71) Applicant (for all designated States except US): THE PROCTER & GAMBLE COMPANY [US/US]; One Procter & Gamble Plaza, Cincinnati, OH 45202 (US). (72) Inventors; and (75) Inventors/Applicants (for US only): MOSS, Michael, Alan, J. [GB/GB]; 46 Park Avenue, Prudhoe NE42 5BB (GB). THOEN, Christiaan, A., J., K. [BE/GB]; 35 Preston Wood, North Shields, Tyne & Wear NE30 3LT (GB). (74) Agents: REED, T., David et al.; The Procter & Gamble Company, 5299 Spring Grove Avenue, Cincinnati, OH 45217 (US).		(81) Designated States: CA, CN, JP, US, VN, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>With international search report.</i>
(54) Title: DETERGENT COMPOSITION (57) Abstract Detergent compositions are disclosed comprising a surfactant, a detergency builder comprising zeolite P having a silicon to aluminium ratio not greater than 1.33 (zeolite MAP); and one or more additional components selected from anionic optical brighteners which are stilbene derivatives; specific polymer dye transfer inhibition agents; and an oxidative catalyst. The compositions may be of any suitable physical form, preferably granular or liquid. Methods of making the compositions are disclosed.		

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TITLE: DETERGENT COMPOSITION

The present invention relates to a detergent composition and, in particular, to improvements in the detergency performance of laundry detergent compositions comprising zeolites as a sequestering agent for water hardness.

Detergent compositions for heavy-duty fabric washing conventionally contain detergency builders which lower the concentration of calcium and magnesium water hardness ions in the wash liquor and thereby provide good detergency effect in both hard and soft water.

Conventionally, inorganic phosphates, such as sodium tripolyphosphate, have been used as builders for laundry detergents. More recently, alkali metal aluminosilicate ion-exchangers, particularly crystalline sodium aluminosilicate zeolite A, have been proposed as replacements for the inorganic phosphates.

For example, EP 21 491A (Procter & Gamble) discloses detergent compositions containing a building system which includes zeolite A, X or P (B) or a

mixture thereof. EP 384070A (Unilever) discloses specific zeolite P materials having an especially low silicon to aluminium ratio not greater than 1.33 (hereinafter referred to as zeolite MAP) and describes its use as a detergency builder. To date, however, zeolite A is the preferred aluminosilicate detergency builder in commercially available products.

EP 384070 (Unilever) suggests that zeolite MAP has certain advantages over zeolite A as a detergency builder. However, we have found that compositions containing zeolite MAP as detergency builder can result in poorer fabric whiteness, as compared with compositions containing zeolite A as detergency builder, in washing loads containing a mixture of coloured and white fabrics.

Surprisingly, we have found that zeolite MAP gives good fabric whiteness performance when used in combination with specific fabric whitening agents and/or specific polymeric materials and/or with an oxidative catalyst.

Thus, the present invention provides a detergent composition comprising:

- a) a surfactant selected from anionic, nonionic, cationic, amphoteric and zwitterionic detergent-active compounds and mixtures thereof;
- b) a detergency builder comprising zeolite P

having a silicon to aluminium ratio not greater than 1.33 (zeolite MAP); and

c) one or more additional components selected from

(i) anionic optical brighteners which are stilbene derivatives;

(ii) polymers selected from polyamine N-oxide polymers, copolymers of N-vinylpyrrolidone and N-vinylimidazole, polyvinylpyrrolidone polymers, polyvinylloxazolidones, polyvinylimidazoles or mixtures thereof; and

(iii) manganese phthalocyanintetrasulphonate.

The detergent composition according to the invention may be of any physical type, for example powders, liquids and gels. However, granular and liquid compositions are preferred.

Preferably the detergent composition according to the present invention contains no bleach.

The detergent composition according to the invention contains, as an essential ingredient, one or more surfactants selected from anionic, nonionic, cationic, amphoteric and zwitterionic detergent-active compounds and mixtures thereof. Such surfactants are well known and described in the literature, for

example, in "Surface-Active Agents and Detergents", Volumes I and II by Schwartz, Perry and Berch.

Examples of suitable anionic surfactants include alkylbenzene sulphonates, particularly sodium linear alkylbenzene sulphonates having an alkyl chain length of C₈-C₁₅; C₁₂-C₁₅ primary alkyl sulphates; olefin sulphonates; alkyl xylene sulphonates; dialkyl sulposuccinates; and fatty acid ester sulphonates. Sodium salts are generally preferred.

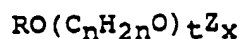
Examples of suitable nonionic surfactants include alkoxylated adducts of fatty alcohols containing an average of from 3 to 10 alkylene oxide groups per molecule.

A particularly preferred aliphatic alcohol ethoxylate is a primary alcohol having an average of from 12 to 15 carbon atoms in the alkyl chain condensed with an average of from five to seven ethoxy groups per mole of alcohol.

Other examples of suitable alkoxylated adducts of fatty alcohols are Synperonic A3 (ex ICI), which is a C₁₃-C₁₅ alcohol with about three ethylene oxide groups per molecule and Empilan KB3 (ex Marchon), which is lauric alcohol 3EO. Mixtures of such ethoxylated alcohols are also contemplated by the present invention.

Another class of nonionic surfactants comprises alkyl polyglucoside compounds of general

formula



wherein Z is a moiety derived from glucose; R is a saturated hydrophobic alkyl group that contains from 12 to 18 carbon atoms; t is from 0 to 10 and n is 2 or 3; x is from 1.1 to 4, the compounds including less than 10% unreacted fatty alcohol and less than 50% short chain alkyl polyglucosides. Compounds of this type and their use in detergent compositions are disclosed in EP-B 0070074, 0070077, 0075996 and 0094118.

The surfactant will generally be included in the detergent composition in an amount of 5 to 60% by weight, preferably 5 to 40% by weight and most preferably from 10 to 25% by weight of the composition.

According to the present invention the detergency builder system is based on zeolite MAP, optionally in conjunction with one or more supplementary builders. The amount of zeolite MAP employed may range, for example, from 5 to 60 wt%, more preferably from 15 to 40 wt%.

Zeolite MAP is described in EP 384070A (Unilever). It is defined as an alkali metal aluminosilicate of the zeolite P type having a silicon to aluminium ratio not greater than 1.33, preferably within the range from 0.9 to 1.33 and more preferably within the range of from 0.9 to 1.2.

Of particular interest is zeolite MAP having a silicon to aluminium ratio not greater than 1.15 and, more particularly, not greater than 1.07.

Zeolite P having a Si:Al ratio of 1.33 or less may be prepared by the following steps:

(i) mixing together a sodium aluminate having a mole ratio $\text{Na}_2\text{O}:\text{Al}_2\text{O}_3$ within the range of from 1.4 to 2.0 and a sodium silicate having a mole ratio $\text{SiO}_2:\text{Na}_2\text{O}$ within the range of from 0.8 to 3.4 with vigorous stirring at a temperature within the range of from 25°C to boiling point usually 95°C, to give a gel having the following composition;

Al_2O_3 : (1.75-3.5) SiO_2 : (2.3-7.5) Na_2O :P (80-450) H_2O ;

(ii) ageing the gel composition for 0.5 to 10 hours, preferably 2 to 5 hours, at a temperature within the range of from 70°C to boiling point, usually to 95°C, with sufficient stirring to maintain any solids present in suspension;

(iii) separating the crystalline sodium aluminosilicate thus formed, washing to a pH within the range of from 10 to 12.5, and drying, preferably at a temperature not exceeding 150°C, to a moisture content of not less than 5 wt%.

Preferred drying methods are spray-drying and flash drying. It appears that oven drying at too high a temperature may adversely affect the calcium binding capacity of the product under certain

circumstances.

Commercial sodium metasilicate pentahydrate dissolved in water and commercial sodium silicate solution (waterglass) are both suitable silica sources for the production of zeolite P in accordance with the invention. The reactants may be added together in any order either rapidly or slowly. Rapid addition at ambient temperature, and slow addition at elevated temperature (90-95°C) both give the desired product.

Vigorous stirring of the gel during the addition of the reactants, and at least moderate stirring during the subsequent ageing step, however, appear to be essential for the formation of pure zeolite P. In the absence of stirring, various mixtures of crystalline and amorphous materials may be obtained.

Zeolite MAP generally has a calcium binding capacity of at least 150 mg CaO per g of anhydrous aluminosilicate, as measured by the standard method described in GB 1473201 (Henkel). The calcium binding capacity is normally 160 mg CaO/g and may be as high 170 mg CaO/g.

Although zeolite MAP like other zeolites contains water of hydration, for the purposes of the present invention amounts and percentages of zeolite are expressed in terms of the notional anhydrous material. The amount of water present in hydrated

zeolite MAP at ambient temperature and humidity is generally about 20 wt%.

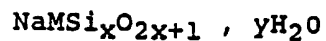
The zeolite MAP used in the present invention preferably has a particle size d_{50} of 1 to 5 micrometres, for example 2.25 to 5 micrometres, particularly 2.75 to 5 micrometres.

The quantity " d_{50} " indicates that 50 wt% of the particles have a diameter smaller than that figure.

According to the invention zeolite MAP may be the sole builder component or it may be used in combination with an organic or inorganic cobuilder. According to a particular embodiment of the invention, zeolite MAP is the principal builder component.

Suitable organic cobuilders can be monomeric or polymeric carboxylates such as citrates or polymers of acrylic, methacrylic and/or maleic acids in neutralised form. Suitable inorganic cobuilders include carbonates and amorphous and crystalline lamellar sodium silicates.

Suitable silicates have the composition:



where M is sodium or hydrogen, preferably sodium; x is a number from 1.9 to 4; and y is a number from 0 to 20. Such materials are described in US Patents No. 4664839; No. 4728443 and No. 4820439 (Hoechst AG).

Especially preferred are compounds in which $x = 2$ and $y = 0$. The synthetic material is commercially available from Hoechst AG as S- $\text{Na}_2 \text{Si}_2\text{O}_5$ (SKS6) and is described in US Patent No. 4664830.

The total amount of detergency builder in the granular composition ranges from 5 to 80 wt%, more preferably from 15 to 60 wt% and most preferably from 10 to 45 wt%.

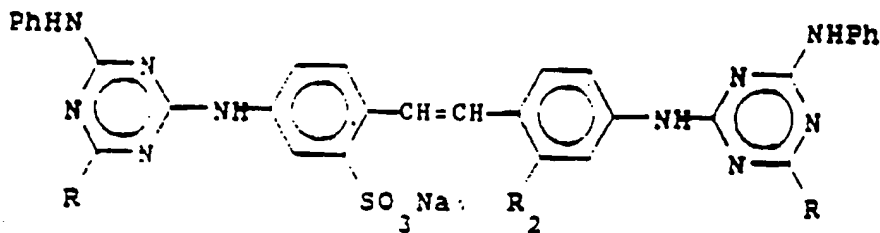
According to the present invention the detergent composition comprises one or more additional components selected from

(i) anionic optical brighteners which are N-bonded stilbene derivatives;

(ii) polymers selected from polyamine N-oxide polymers, copolymers of N-vinylpyrrolidone and N-vinylimidazole, polyvinylpyrrolidone polymers, polyvinylloxazolidones, polyvinylimidazoles or mixtures thereof; and

(iii) manganese phthalocyanintetrasulphonate.

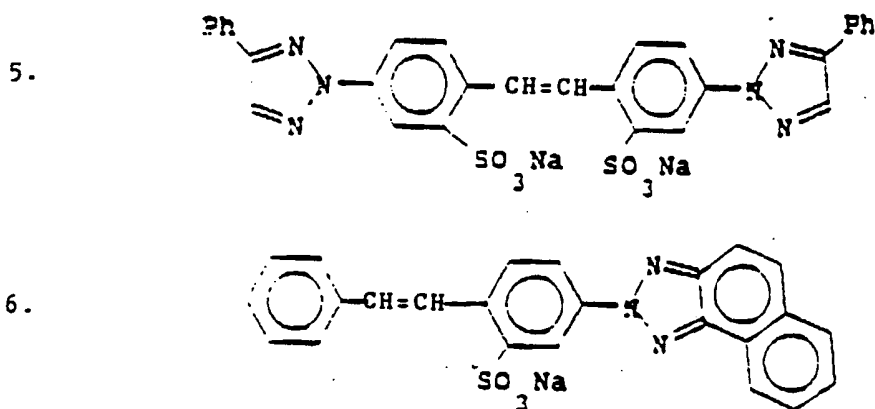
Examples of suitable anionic optical brighteners are compounds of the formula:



wherein

1. R = diethanolamino and $R_2 = \text{SO}_3\text{Na}$;
2. R = morpholino and $R_2 = \text{SO}_3\text{Na}$;
3. R = anilino, $R_2 = \text{SO}_3\text{Na}$ or H; and
4. R = 1-methyl-2-hydroxethylamino, $R_2 = \text{SO}_3\text{Na}$.

Examples of less preferred anionic optical brighteners include compounds of the formula:



Compounds of formulae 1-4 above are preferred. The optical brightener is suitably incorporated in the composition in an amount of from 0.01 to 5.0 wt%, preferably in an amount of from 0.05 to 0.3 wt%.

Alternatively, or in addition, the detergent composition according to the invention includes a polymer. The polymers act as dye-transfer inhibiting agents by inhibiting the transfer of dyes from coloured fabrics onto fabrics washed therewith. These polymers

have the ability to complex or adsorb the fugitive dyes washed out of dyed fabrics before the dyes have the opportunity to become attached to other articles in the wash.

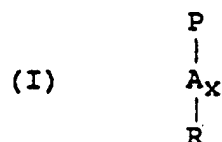
Suitable polymers are polyamine N-oxide polymers copolymers of N-vinylpyrrolidone and N-vinylimidazole, polyvinylpyrrolidone polymers, polyvinylloxazolidones and polyvinylimidazoles or mixtures thereof.

The detergent composition may suitably comprise from 0.001 to 10 wt%, preferably from 0.01 to 2 wt% and most preferably from 0.05 to 1 wt% of the polymer.

Suitable polymers for use in the detergent composition according to the invention are described in detail in the following.

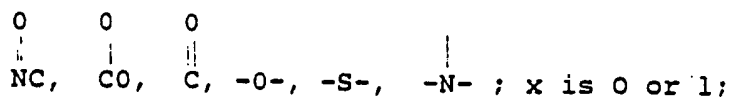
a) Polyamine N-oxide polymers

The polymer N-oxide polymers suitable for use may contain units having the following structure formula :



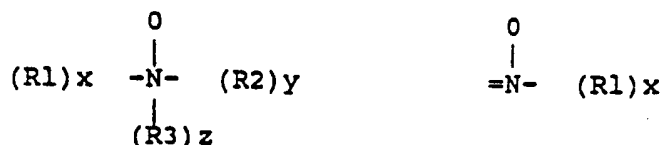
wherein P is a polymerisable unit, wherein the R-N-O group can be attached to or wherein the R-N-O group forms part of the polymerisable unit or a combination of both.

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R are aliphatic, ethoxylated aliphatics, aromatic, heterocyclic or alicyclic groups or any combination thereof wherein the nitrogen of the N-O group can be attached or wherein the nitrogen of the N-O group is part of these groups.

The N-O group can be represented by the following general structure :



wherein R1, R2, and R3 are aliphatic groups, aromatic, heterocyclic or alicyclic groups or combinations thereof, x or/and y or/and z is 0 or 1 and wherein the nitrogen of the N-O group can be attached or wherein the nitrogen of the N-O group forms part of these groups.

The N-O group can be part of the polymerisable unit (P) or can be attached to the polymeric backbone or a combination of both.

Suitable polyamine N-oxides wherein the N-O group forms part of the polymerisable unit comprise polyamine N-oxides wherein R is selected from aliphatic, aromatic, alicyclic or heterocyclic groups.

One class of said polyamine N-oxides comprises the group of polyamine N-oxides wherein the nitrogen of the N-O groups forms part of the R-group. Preferred polyamine N-oxides are those wherein R is a heterocyclic group such as pyrridine, pyrrole, imidazole, pyrrolidine, piperidine, quinoline, aridine and derivatives thereof.

Another class of said polyamine N-oxides comprises the group of polyamine N-oxides wherein the nitrogen of the N-O group is attached to the R-group.

Other suitable polyamine N-oxides are the polyamine oxides wherein the N-O- group is attached to the polymerisable unit. Preferred classes of these polyamine N-oxides are the polyamine N-oxides having the general formula (I) wherein R is an aromatic, heterocyclic or alicyclic group wherein the nitrogen of the N-O functional group is part of said R group.

Examples of these classes are polyamine oxides wherein R is a heterocyclic compound such as pyrridine, pyrrole, imidazole and derivatives thereof. Another preferred class of polyamine N-oxides are the polyamine oxides having the general formula (I) wherein R are aromatic, heterocyclic or alicyclic groups wherein the nitrogen of the N-O functional group is attached to said R groups.

Examples of these classes are polyamine oxides wherein the R groups can be aromatic such as

phenyl.

Any polymer backbone can be used as long as the amine oxide polymer formed is water-soluble and has dye transfer inhibiting properties. Examples of suitable polymeric backbones are polyvinyls, polyakylenes, polyesters, polyethers, polyamide, polyimides, polyacrylates and mixtures thereof.

The amine N-oxide polymers of the present invention typically have a ratio of amine to the amine N-oxide of 10:1000000. However the amount of amine oxide groups present in the polyamine oxide polymer can be varied by appropriate copolymerisation or by appropriate degree of N-oxidation. Preferably, the ratio of amine to amine N-oxide is from 2:3 to 1:1000000. More preferably from 1:4 to 1:1000000, most preferably from 1:7 to 1:1000000. The polymers of the present invention actually encompass random or block copolymers where one monomer type is an amine N-oxide and the other monomer type is either an amine N-oxide or not. The amine oxide unit of the polyamine N-oxides has a $Pka < 10$, preferably $Pka < 7$, more preferred $Pka < 6$.

The polyamine oxides can be obtained in almost any degree of polymerisation. The degree of polymerisation is not critical provided the material has the desired water-solubility and dye-suspending power.

phenyl.

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The polyamine oxides can be obtained in almost any degree of polymerisation. The degree of polymerisation is not critical provided the material has the desired water-solubility and dye-suspending power.

Typically, the average molecular weight is within the range of 500 to 100,000; preferably from 1,000 to 50,000, more preferably from 2,000 to 30,000, most preferably from 3,000 to 20,000.

According to a particular aspect of the invention the detergent composition comprises from 0.01 to 1.5 wt% of polyvinylpyridine N-oxide.

b) Copolymers of N-vinylpyrrolidone and N-vinylimidazole

The N-vinylimidazole-N-vinylpyrrolidone polymers used in the present invention have an average molecular weight range from 5,000 - 1,000,000, preferably from 20,000 - 200,000.

Highly preferred polymers for use in detergent compositions according to the present invention comprise a polymer selected from N-vinylimidazole-N-vinylpyrrolidone copolymers wherein said polymer has an average molecular weight range from 5,000 to 50,000 more preferably from 8,000 to 30,000, most preferably from 10,000 to 20,000.

The average molecular weight range was determined by light scattering as described in Barth H.G. and Mays J.W. Chemical Analysis Vol 113, "Modern Methods of Polymer Characterization".

Highly preferred N-vinylimidazole-N-vinylpyrrolidone copolymers have an average molecular

weight range from 5,000 to 50,000; more preferably from 8,000 to 30,000; most preferably from 10,000 to 20,000.

The N-vinylimidazole-N-vinylpyrrolidone copolymers characterised by having said average molecular weight range provide excellent dye transfer inhibiting properties while not adversely affecting the cleaning performance of detergent compositions formulated therewith.

The N-vinylimidazole-N-vinylpyrrolidone copolymer of the present invention has a molar ratio of N-vinylimidazole to N-vinylpyrrolidone from 1 to 0.2, more preferably from 0.8 to 0.3, most preferably from 0.6 to 0.4.

According to a particular aspect of the invention the detergent composition comprises from 0.01 to 1.5 wt% of polyvinylpyrrolidone-polyvinylimidazole copolymer.

c) Polyvinylpyrrolidone

The detergent compositions of the present invention may also utilize polyvinylpyrrolidone ("PVP" having an average molecular weight of from about 2,500 to about 400,000, preferably from about 5,000 to about 200,000, more preferably from about 5,000 to about 50,000, and most preferably from about 5,000 to about 15,000. Suitable polyvinylpyrrolidones are commercially available from ISP Corporation, New York,

NY and Montreal, Canada under the product names PVP K-15 (viscosity molecular weight of 10,000), PVP K-30 (average molecular weight of 40,000), PVP K-60 (average molecular weight of 160,000), and PVP K-90 (average molecular weight of 360,000). PVP K-15 is also available from ISP Corporation. Other suitable polyvinylpyrrolidones which are commercially available from BASF Corporation include Sokalan HP 165 and Sokalan HP 12. Polyvinylpyrrolidones known to persons skilled in the detergent field: see for example EP-A-262,897 and EP-A-256,696 are also suitable. According to a particular aspect of the invention the detergent composition comprises from 0.05 to 3.0 wt%, preferably from 0.1 to 0.3 wt% of PVP.

d) Polyvinylloxazolidone :

The detergent compositions of the present invention may also utilize polyvinylloxazolidone as a polymeric dye transfer inhibiting agent. Said polyvinylloxazolidones have an average molecular weight of from about 2,500 to about 400,000, preferably from about 5,000 to about 200,000, more preferably from about 5,000 to about 50,000, and most preferably from about 5,000 to about 15,000.

e) Polyvinylimidazole :

The detergent compositions of the present invention may also utilize polyvinylimidazole as polymeric dye

transfer inhibiting agent. Said polyvinylimidazoles have an average MV about 2,500 to about 400,000, preferably from about 5,000 to about 200,000, more preferably from about 5,000 to about 50,000, and most preferably from about 5,000 to about 15,000.

The detergent composition according to the invention may include the conventional detergent materials. However, preferably the composition is free of bleach. Other optional materials which may be present include, for example, enzymes, fluorescers, antiredeposition agents, inorganic salts such as sodium sulphate, lather control agents, fabric softening agents, pigments, coloured speckles and perfumes.

The detergent compositions of the invention may be prepared by any suitable method. The particulate detergent compositions are suitably prepared by any tower (spray-drying) or non-tower process.

In processes based around a spray-drying tower, a base powder is first prepared by spray-drying a slurry and then other components unsuitable for processing via the slurry can be sprayed on or admixed (postdosed).

The zeolite MAP is suitable for inclusion in the slurry, although it may be advantageous for processing reasons for part of the zeolite MAP to be incorporated post-tower.

Alternatively, particulate detergent compositions in accordance with the invention may be prepared by wholly non-tower processes such as granulation.

The granular detergent compositions of the invention may be prepared to any suitable bulk density. The compositions preferably have a bulk density of at least 400 g/l preferably at least 550 g/l, most preferably at least 700 g/l and, with particular preference at least 800 g/l.

The benefits of the present invention are particularly evident in powders of high bulk density, for example, of 700 g/l or above. Such powders may be prepared either by post-tower densification of spray-dried powder, or by wholly non-tower methods such as dry mixing and granulation; in both cases a high-speed mixer/granulator may advantageously be used. Processes using high-speed mixer/granulators are disclosed, for example, in EP340 013A, EP 367 339A, EP 390 251A and EP 420 317A (Unilever).

According to one aspect of the invention there is provided a granular detergent composition comprising:

from 5 to 60 wt%, preferably 5 to 40 wt%, of component (a) defined hereinbefore;

from 10 to 80 wt% of component (b) defined hereinbefore; and

from 0.001 to 10 wt% of component (c) defined hereinbefore.

According to another embodiment of the invention there is provided a liquid detergent composition, preferably a heavy duty liquid detergent composition, comprising from 5 to 60 wt% of component (a) above and from 5 to 40 wt% of component (b) above and from 0.001 to 10 wt% of component (c) above.

According to this embodiment the liquid detergent composition may be of any convenient physical form which may be aqueous or anhydrous. The term "liquid" used herein includes partly viscous formulations such as gels. The liquid detergent composition generally has a pH of from 6.5 to 10.5.

The total amount of detergency builder in the liquid composition is preferably from 5 to 70% of the total liquid composition.

The following Examples provide illustrative detergent compositions according to the present invention.

The following abbreviations have been used:

LAS	-	linear C ₁₂ alkyl benzene sulphonate
AS	-	sodium alkyl sulphate
TAS	-	sodium tallow alcohol sulphate
45E7	-	C ₁₄₋₁₅ primary alcohol condensed with an average of 7 moles of ethylene oxide
25E3	-	C ₁₂₋₁₅ primary alcohol condensed with

an average of 3 moles of ethylene oxide

PC3	-	percarbonate
PB1	-	perborate monohydrate
PB4	-	perborate tetrahydrate
TAED	-	Tetraacetyl ethylene diamine
PVP	-	polyvinyl pyrrolidone
PYNO	-	polyvinylpyridine N oxide
PVPV1	-	polyvinylpyrrolidone-polyvinylimidazole copolymer
MnPC	-	manganese phthalocyanintetrasulphonate.
EDTMP	-	ethylene diamine tetramethylene phosphonate
CMC	-	carboxymethyl cellulose

Brighteners 1, 2 and 3 correspond to the compounds of formulae 1, 2 and 3 respectively as defined in the description.

Examples

	1	2	3	4
LAS	-	7	-	5
C ₄₅ AS	7	-	-	-
C ₂₄ AS	-	-	5.6	3
TAS	-	5	-	-
45E7	7	4	6	5
25E3	-	-	2	-
Glucamide	-	-	-	5
Zeolite MAP	38	32	40	35
Na SKS-6	5	-	-	-
citrate	10	12	-	10
carbonate	7	7	10	10
silicate (2.0 ratio)	-	6	5	5
PC3	14	-	-	-
PB1	-	10	-	-
PB4	-	5	-	2
TAED	2.5	3	-	-
Protease (Alcalase)	2.0	2.0	2.0	2.0
Amylase (Termamyl)	0.4	0.4	0.4	0.4
Lipase (Lipolase)	0.4	0.4	0.4	0.4
PVP	1.0	-	-	-

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PVNO	-	0.5	-	-
PVPVI	-	-	0.5	-
MnPC	-	-	-	0.2
EDTMP	0.1	0.2	0.1	0.1
CMC	0.8	0.6	0.8	0.8
Suds Suppressor				
Brightener 1	-	0.2	-	-
2	0.2	-	0.2	-
3	-	-	-	0.2
Moisture, sulphate and miscellaneous	<u>6.6</u> <u>100</u>	<u>4.7</u> <u>100</u>	<u>27.0</u> <u>100</u>	<u>15.9</u> <u>100</u>

CLAIMS

1. A detergent composition comprising:
 - a) a surfactant selected from anionic, nonionic, cationic, amphoteric and zwitterionic detergent-active compounds and mixtures thereof;
 - b) a detergency builder comprising zeolite P having a silicon to aluminium ratio not greater than 1.33 (zeolite MAP); and
 - c) one or more additional components selected from
 - (i) anionic optical brighteners which are N-bonded stilbene derivatives;
 - (ii) polymers selected from polyamine N-oxide polymers, copolymers of N-vinylpyrrolidone and N-vinylimidazole, polyvinylpyrrolidone polymers, polyvinylloxazolidones, polyvinylimidazoles or mixtures thereof; and
 - (iii) manganese phthalocyanintetrasulphonate.
2. A detergent composition according to claim

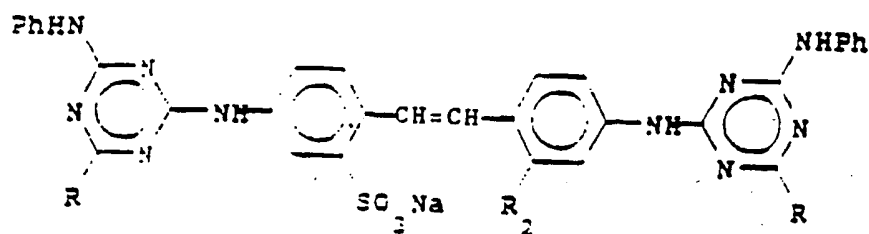
1, wherein the zeolite MAP has a silicon to aluminium ratio not greater than 1.07.

3. A detergent composition according to claim 1 or 2, wherein the zeolite MAP has a particle size d_{50} of 1 to 5 micrometres.

4. A detergent composition according to any one of claims 1 to 3, which comprises 5 to 60 wt% of the zeolite MAP.

5. A detergent composition according to claim 4 which comprises from 10 to 40 wt% of the zeolite MAP.

6. A detergent composition according to any one of claims 1 to 5, wherein the optical brightener (c)(i) is selected from compounds of the formula:



wherein R represents diethanolamino and R_2 represents $-SO_3Na$; or R represents morpholino and R_2 represents $-SO_3Na$; or R represents anilino and R_2 represents H or $-SO_3Na$; or R represents 1-methyl-2-hydroxyethylamino and R_2 represents $-SO_3Na$.

7. A detergent composition according to any one of claims 1 to 6 which comprises one or more optical brighteners in an amount of from 0.001 to 10.0 wt% of the composition.

8. A detergent composition according to claim 7, which comprises one or more optical brighteners in an amount of from 0.05 to 0.3 wt% of the composition.

9. A detergent composition according to any one of claims 1 to 8, wherein the polymer (c)(ii) is selected from polyvinylpyrrolidone; polyvinylpyridine N-oxide; and polyvinylpyrrolidone-polyvinylimidazole copolymer.

10. A detergent composition according to claim 9, wherein the polymer (c)(ii) comprises polyvinylpyrrolidone in an amount of from 0.05 to 0.3 wt% based on the composition.

11. A detergent composition according to claim 9 wherein the polymer (c)(ii) comprises polyvinylpyridine N-oxide or polyvinylpyrrolidone-polyvinylimidazole copolymer in an amount of from 0.01 to 1.5 wt% based on the composition.

12. A detergent composition according to any one of claims 1 to 11, in which component (c) comprises the manganese phthalocyanintetrasulphonate in an amount of from 0.01 to 1.0 wt% based on the composition.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US95/02699

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) : C11D 3/12, 3/37, 3/42

US CL : 252/ 547, 543, 174.23, 174.25

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 252/ 547, 543, 174.23, 174.25

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

Please See Extra Sheet.

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	EP, A, 0,384,070 (UNILEVER NV) 28 August 1990, Abstract, page 4, lines 1-44, page 8, lines 35-42, page 9, lines 22-30.	1-11
Y	WO, A, 94/01520 (PROCTER & GAMBLE) 20 January 1994 Abstract, page 3, 3rd paragraph, page 7, 4th paragraph.	1-5, 7-11
Y	EP, A, 0 587 550 (PROCTER & GAMBLE) 16 March 1994, Abstract, page 3, lines 5-57, page 9, lines 30-33, page 12, line 52 - page 13, line 1.	1-9, 11
A	US, A, 4,417,994 (STODDART) 29 November 1983, col. 2, lines 18-63.	1 and 12

☒ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:	* T	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
* A* document defining the general state of the art which is not considered to be of particular relevance	* X*	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
* E* earlier document published on or after the international filing date	* Y*	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
* L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	* &*	document member of the same patent family
* O* document referring to an oral disclosure, use, exhibition or other means		
* P* document published prior to the international filing date but later than the priority date claimed		

Date of the actual completion of the international search

15 MAY 1995

Date of mailing of the international search report

16 JUN 1995

Name and mailing address of the ISA/US
Commissioner of Patents and Trademarks
Box PCT
Washington, D.C. 20231

Facsimile No. (703) 305-3230

Authorized officer

ERIN HARRIMAN

Telephone No. (703) 308-0661

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US95/02699

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US, A, 4,400,173 (BEAVAN) 23 August 1983, col. 2, lines 24-64.	1 and 12
A	US, A, 4,399,049 (GRAY ET AL.) 16 August 1983, col. 8, lines 21-64.	1 and 12

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US95/02699

B. FIELDS SEARCHED

Electronic data bases consulted (Name of data base and where practicable terms used):

APS, REG. CAS

search terms: manganese phthalocyanine tetrasul(fonic phonic fonate phonate), polyvinylpyrrolidone, stilbene, brighten?, zeolite#

